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Study of material behavior in DAC: system Si-O (SiO_x) and compound $Fe_{78}Mn_{20}Si_2$

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ABSTRACT

For the last ten years or so, the gasketed diamond anvil cell (DAC) has become the standard tool for the generation of high pressures. Compared with the classic hydraulic piston-cylinder devices, a DAC is three to four orders of magnitude less massive, and will generate static pressures one to two orders of magnitude higher than previous devices.

In this paper, we attempt to give an understanding of the gasket behavior which will be helpful to the worker requiring routine and reliable use of a DAC in the submegabar pressure range.

Keywords: diamond anvil cell, gasket, material behavior, phase and structure transitions.

1.INTRODUCTION

The diamond anvil cell (DAC) became a widely used tool due to the application of the ruby method for pressure determination and the possibility of obtaining quasi-static high pressure. [1,2] But for the compression of solids the non-uniformity of pressure is accompanied by the efficiency reduction of a high pressure apparatus due to the elastic deformation of the anvils at higher pressure. In practice, the methods of quasi-static pressure generation by applying deformable metal gasket containers for a sample, ruby gauge and pressure-transmitting media help to eliminate the above mentioned drawbacks. At the same time the pressure generation in a DAC with a metal gasket depends substantially on the gasket geometry and character of the elastic-plastic deformation of the gasket material.

2. THE MATHEMATICAL MODEL OF GASKET BEHAVIOR IN DAC

One of the basis parameters of pressure character in a gasket operating volume is the degree of reduction of the initial gasket thickness under axial load. Experimental data on the pressure value $P_{r=0}$ (acting upon the gasket center) in dependence on the T301 steel gasket thickness h μm are presented in Fig.1.

The experimental curve $P_{r=0}(h)$ shows three basis types of stress-strain state within the central gasket part under compression between the anvils: the elastic-plastic deformation state (pressure range 0 - ~5 GPa); the plastic flow state (~ 5 - ~ 40 GPa); the volumetric triaxial compression state (≥ 40 GPa).

The analytical solving of the stress-pressure-strain distribution problem (in the gasket) is quite difficult. That is why we consider the gasket operation, when it is used for pressure generation, by approximate methods. Pressure in the gasket within the elastic deformation area may be calculated according to the relation given by Prins [4]:

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$$P = -\int_{h_0}^{h} \frac{dh}{Ch}, \qquad (1)$$

where C is the materials compressibility, h_0 is the initial gasket thickness. With the axial load increase on the diamond anvils the gasket material starts to deform. Thus the pressure acting upon the gasket center within the plastic flow area may be calculated by the formula given by Prins [4]:

$$P_{r=0} = \sigma_z \left(e^{2\mu b/h} - 1\right), \qquad (2)$$

where σ_z is the axial stress (initial pressure) at which plastic flow of the gasket material occurs, μ is the friction coefficient, b is the radius of the operation butt end of the anvil. For a further increase in load the flow of the gasket material from the center to the periphery stops and the pressure at the gasket center under uniform compression is calculated by an equation like Eq.(1):

$$P_{r=0} = -\int_{h_0'}^{h} \frac{dh}{Ch}, \qquad (3)$$

where h'_0 is the efficient initial gasket thickness after the plastic flow stoppage.

The analytical dependencies of $P_{r=0}(h)$ describing all the main stress-strain state areas are calculated for the parameter values of the T301 steel gasket and for the anvils of the octahedron type of diamond single crystals: $C = 0.69\times10^{-5}$ MPa; $h_0 = 250$ μm; $h_0' = 50$ μm; $\sigma_z = 1000$ MPa; $\mu = 0.25$; $b = 300$ μm; (Fig. 1, curves 2, 3, 6). The values of h_{cr} and P_{max} are calculated as follows: $h_{cr} = (2\mu/\alpha)b$, $P_{max} = \sigma_z(e^{\alpha} - 1)$, where α is a parameter determined by the properties of the gasket material. In our case $h_{cr} = 40$ μm, $P_{max} = 41$ GPa, $\alpha = 3.75$. It may be seen from a comparison of the experimental dependence with the theoretical curves $P_{r=0}(h)$, Fig. 1, that the application of the given analytical expressions describing the behavior of the deformable gasket gives rise to serious objections because of the discordance between the analytical dependence $P_{r=0}(h)$, Fig. 1, curve 3, and the experimental curve, Fig. 1, curve 1, during the elastic-plastic deformation of the gasket.

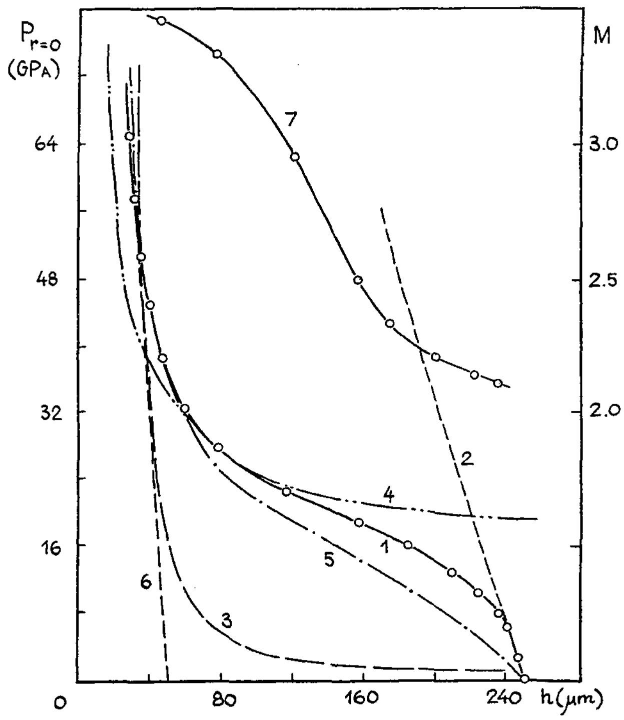


Fig.1. Relation between pressure $P_{r=0}(1-6)$ on the gasket axis and multiplication coefficient M(7) and the deformable gasket thickness h: 1- experiment; 2-6 -calculation

Efros[5,6] have suggested that other analytical expressions describing the gasket behavior should be used for the generation of pressure in the *DAC*. According to model 1, the mean pressure p of the gasket-sample may be evaluated by the relation given by Samanta [7]:

$$\frac{\bar{p}}{2k}=1+\frac{1+\sec\theta}{2}\left[\left(1+\frac{2b}{h}\mathrm{tg}\theta\right)\times\ln\left(1+\frac{h}{2b}\mathrm{ctg}\theta\right)-1\right]+\frac{b}{3h}+\frac{\mathrm{tg}\theta}{2}+\frac{h}{b}+\frac{\sec\theta\,\mathrm{cosec}\theta}{2}, \quad (6)$$

where k is the shear yield strength of the gasket material, θ is the shape variation angle of the diametrical gasket cross-section (θ = 36 - 40°), b is the operating butt end radius of the anvil.

According to the model 2, suggested by Ilyushin[8], we may evaluate the unit pressure p generated in the gasket-container as

$$p=\begin{cases}1+q+\dfrac{2}{\sqrt{3}h}(r-a) & \text{at} \quad a\le r\le r_0\\[2ex] 1+m+\dfrac{2}{\sqrt{3}h}(b-r) & \text{at} \quad r_0\le r\le b\end{cases},$$

where a is the gasket operating cell radius, q is the operating cell pressure (at $a = 0$, $q = P_{r=0}$), $r_0 = \frac{1}{4}\sqrt{3}\,h\,(m - \bar{q}) \frac{1}{2}(b+a)$ is the radius of a circle along which the pressure is maximum, $\bar{q} = q/\sigma_s$, b is the operating butt end radius of the anvil, m is a parameter representing the support from that part of the gasket which is out of the anvil.

The dependences of $P_{r=0}(h)$ calculated by model 1 and 2 describe the behavior of the T301 steel gasket (Fig. 1, curves 4 and 5). Comparison of the experimental dependence $P_{r=0}(h)$, Fig. 1, curve 1, with the theoretical curves, Fig. 1, curves 4 and 5, shows the existence of discordance, though it is smaller than that obtained by the relations suggested by Prins [4] (Fig. 1, curve 3).

The following parameters most easily monitored during operation of the *DAC* are the force Q applied to the cell, the pressure P generated, the gasket operating cell radius a and thickness h. The dependence $P(Q)$ (the dependencies $a(P)$ and $h(P)$) turns out to be very useful as a diagnostic tool, and so we calculate it here by model 2 (Fig. 2 and 3). For each experiment to be carried out in a *DAC*, the geometry and properties of gasket may be selected differently according to the pressure range required. The sample size, and the number of pressure cycles required.

3. HIGH PRESSURE EFFECT ON PHASE AND STRUCTURE TRANSITIONS

High pressure structural studies are important not only to test various physical theories and thereby improve our theoretical understanding of solids, or to map out phase diagrams in pressure, volume, temperature- space, but in terms of producing new, and possible better materials as well.

DAC has revolutionised high pressure experiment in the pressure range above $P \approx 1$ GPa. The DAC can be used either with a hole or without one in gasket between the diamond anvils.

3.1. The gasket-container: system Si-O

Extensive experimental studies of the group-IV elements Si and Ge have been made in recent years. Motivations have included the rich variety of phase transitions. Si shows the following phase-transition sequence in the pressure range 0-50 GPa [9-11]: cubic diamond to β-Sn at 11 GPa; β-Sn to simple hexagonal (*SH*) at 13-16 GPa; *SH* to an intermediate phase at 34 GPa and finally to hexagonal close packed (*HCP*) above 40 GPa.

In spite of considerable efforts done in above area, the structural systematic of the group-IV and related semiconductors still demands to be clarified. Moreover, practically nothing is known about possible effects of dopants or impurities on pressure-induced phase transitions, even in the case of the best investigated material, silicon. However, also from the last

published data on the phase behaviour of Si nanocrystallites coated with SiO_2 it follows that such dopant- related effects are highly probable to exist. A considerable increase of the transition pressure (from 11GPa to approximately 22GPa) in the diamond to -β- Sn phase transition has been observed in Si nanocrystals as compared to the case of bulk Si. This increase in the transition pressure is ascribed to a low density of defect nucleation sites for phase transformation in Si nanocrystals as compared to that in the bulk material. A quite opposite situation (large concentration of the mentioned nucleation sites) would exist in case of heavy doped materials. A representative example would be the system Si – O (SiO_X): Czochralski grown silicon, Cz-Si, in which oxygen atoms are typically present in form of interstitials O_i, with a concentration up to more than 10^{18} cm^{-3}. These atoms are clustering/transforming at higher temperatures (pressures) creating different oxygen – related defects, also clusters and precipitates with a SiO_{2-x} composition.[12]
One can reasonable assume that such "secondary defects" would create a lot of additional nucleation sites, so promoting the pressure – induced diamond – to – β- Sn phase transition. The increase of defect concentration in the *HP* - (*HT*) treated Cz-Si samples with initially present SiO_{2-x} precipitates can be considered as a proof of *HP*-induced massive creation of defects on before-created oxygen-related defects. [13,14]

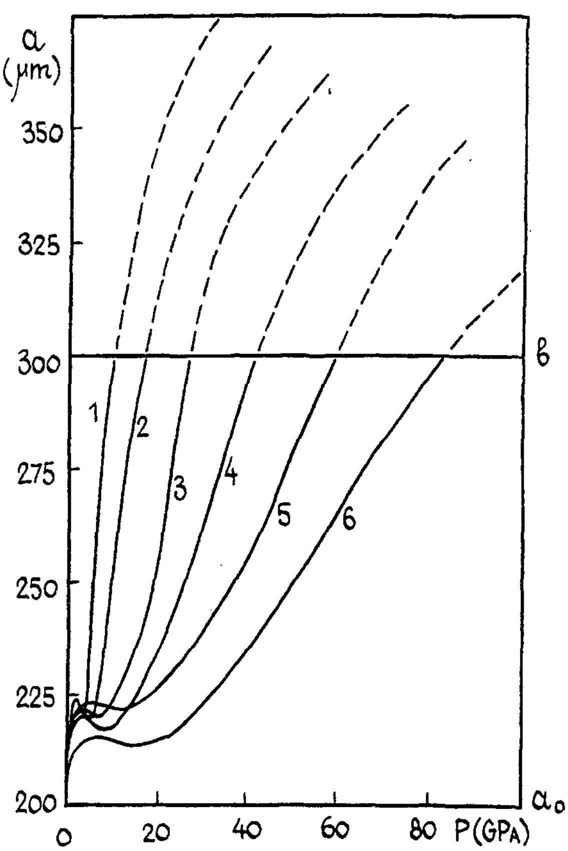


Fig.2

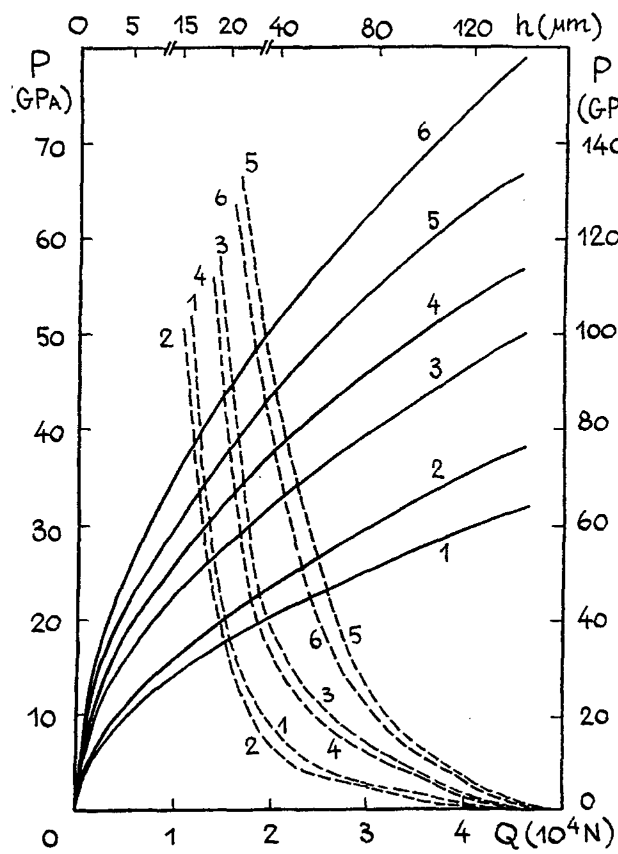


Fig.3

Fig.2. Pressure *P* -force *Q* and pressure *P* – thickness *h* plots for different values of yield stress $YS_{0.2}$ and radius of gasket hole a_0 (h_0 = 150 μm and *b* = 300 μm): 1 - $YS_{0.2}$ = 200 MPa, a_0 = 200 μm; 2 - 200 MPa, 150 μm; 3 - 500 MPa, 200 μm; 4 - 500 MPa, 150 μm; 5 - 1000 MPa, 200 μm; 6 - 1000 MPa, 150 μm

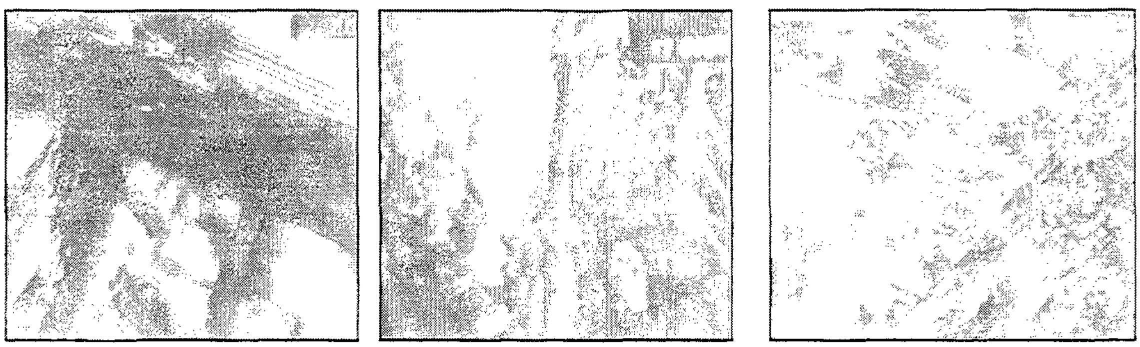
Fig. 3. Radius of gasket hole *a* - pressure *P* plots for different values of yield stress $YS_{0.2}$ and initial thickness of gasket h_0 (a_0 = 200 μm and *b* = 300 μm): 1- $YS_{0.2}$ = 200 MPa, h_0 = 200 μm; 2 – 200 MPa, 150 μm; 3 – 500 MPa, 200 μm; 4 – 500 MPa, 150 μm; 5 – 1000 MPa, 200 μm; 6 – 1000 MPa, 150 μm

3.2. The gasket-sample: compound $Fe_{78}Mn_{20}Si_2$

The characteristic feature of studied compound is the development of strain/baric-induced martensitic transitions $(\gamma+\varepsilon)\rightarrow\varepsilon',\alpha'$. [15]

At investigation of the structure for compound $Fe_{78}Mn_{20}Si_2$ in dependence on the gasket compression degree ε one can differ two types of the substructure (Fig.4). The first (I) is characterised by thin plates of HCP ε–phase in FCC γ-matrix along two or three-intersection plane $\{111\}_\gamma$ (Fig. 4,b). The second (II) is characterised by availability of large plates of ε–phase usually along one plane from the system $\{111\}_\varepsilon$ in which BCC α'–crystals of lath shape are arranged, having alike orientation or forming structural complex "frame"- type (Fig.4c). Increasing of the degree ε by the *DAC* technique as well as decreasing of the radius in the region of compression of a gasket-sample of compound $Fe_{78}Mn_{20}Si_2$ results in the growth of type I-structure. Besides, in the deformed substructure $\varepsilon>30\%$ together with reduction of α'–phase as a result of suppression of martensitic transition $(\gamma+\varepsilon)\rightarrow\alpha'$ and with appearance of new plates of ε'–phase as a result of shift of the dynamic balance $\gamma\leftrightarrow\varepsilon$ in direction of activation of $(\gamma+\varepsilon)\rightarrow\varepsilon'$-transition at loading in DAC we revealed also twins of deformation in ε–phase of types: $\{1012\}_\varepsilon$ and $\{1011\}_\varepsilon$.

Thus the obtained results prove that the specific features of the stressed state (η factor, where $\eta=\sigma/T$, where $\sigma=-P$, T-tangential stress) at which the loading in DAC of metastable materials is carried out can considerably influence on processes of phase and structure transitions and thus cause as a result the desirable level of physico-mechanical properties of materials[16]. The considered dependencies for the factor of the stressed state $\eta(\varepsilon)$ at deformation under pressure of compound $Fe_{78}Mn_{20}Si_2$ by the *DAC* method makes it possible to consider that the intensity of martensitic $(\gamma+\varepsilon)\rightarrow\varepsilon,\alpha'$-transitionsis determined by two competing processes: increase of degree ε ($(\gamma+\varepsilon)\rightarrow\varepsilon,\alpha'$-transitions) and decrease of the factor η ($\eta<0$) (increase *P*) ($(\gamma+\varepsilon)\rightarrow\varepsilon$ and $(\gamma+\varepsilon)\leftarrow\alpha'$-transitions) (Fig.5).



a b c

Fig. 4. Structural changes of gasket compound $Fe_{78}Mn_{20}Si_2$ at DAC loading (x 27000): a - $\varepsilon\approx 0\%$, $P_{r=0}\approx 0.1$ MPa; b – 75%, 28 GPa ($r = 0$); c – 75%, 28 GPa ($r = b$)

4. CONCLUSION

The preliminary analysis carried out on the stress-strain of the metal gasket being used in the *DAC* shows the exceptional importance of the stage of gasket material plastic flow in generating high pressure. Besides, the study of this problem helps not only to characterize the optimum conditions of high pressure generation, but also to obtain information on the phase and structure transformations and rheologic properties of solids (gasket-sample and gasket-container) under high pressure.

The obtained experimental and theoretical results makes it possible to choose the optimum of gasket parameters and properties for the deformable containers, thus providing the submegabar pressure generation functions and the support of the diamond anvils peripheral area.

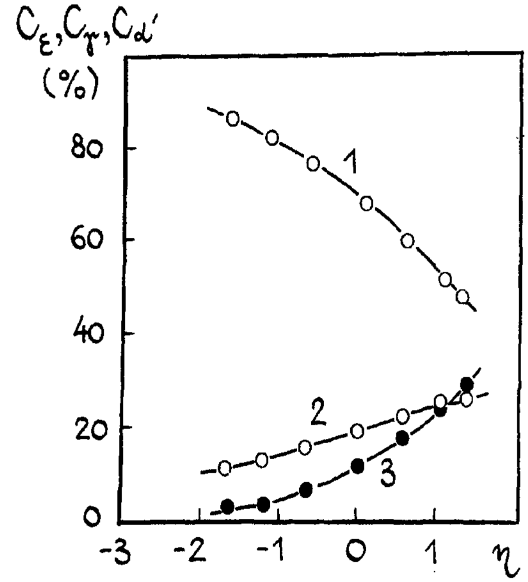


Fig.5. Phase composition in the compound $Fe_{78}Mn_{20}Si_2$ in dependence on the index η: 1 –C_ε; 2- C_γ ; 3- $C_{\alpha'}$

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